Immobilized Grubbs catalysts on mesoporous materials: New insights into support characteristics and their impact on catalytic activity and product selectivity

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Since the discovery of ordered mesoporous silica (OMS), this research area has developed greatly over the years leading to materials with unique opportunities for applications in heterogeneous catalysis. These porous structures have proven to be great supports for homogeneous catalysts in e.g. metathesis. Recently a new, elegant and practical immobilization strategy of Hoveyda-Grubbs complexes on silica supports was reported by Van Berlo *et al.* [1]. Later, this adsorption concept was studied and expanded successfully by others on ordered mesoporous materials (e.g. MCM-41, SBA-15) [2-6].

In search for the ideal catalyst for the ring-opening metathesis polymerization (ROMP) of cyclooctene, we extended this research area by investigating in detail the impact of textural and structural parameters of ordered mesoporous supports. The ideal characteristics of a support for the immobilization of the Hoveyda-Grubbs 2nd generation catalyst (HG 2) in the ROMP of cyclooctene were defined. Immobilized MCM-41 and TUD-1 fulfill these demands and approach the activity of the homogeneous complex.

A thermal treatment of the support to remove physisorbed water seems crucial in obtaining a high activity. The effect of the loading of Ru on the support was smaller. A high loading of Ru (2 wt%) did not affect the activity of HG2/TUD-1, but due to the smaller pore system of MCM-41, this material was more affected by pore diffusion limitations; a lower active site density is preferential with this support.

With an optimized catalytic system, the emphasis was placed on obtaining a high selectivity to C16-C56 cyclic oligomers, valuable intermediates in e.g. the lubricant and fragrance industry. The reaction mechanism of the ring-opening ring-closing metathesis of cyclooctene was studied under heterogeneous conditions and unraveled by carefully evaluating the total mass balance. By performing at low monomer concentrations (0.05 M), working under a kinetic regime (low active site density), and at full conversion, selectivities of 70 % to the C16-C56 cyclic oligomeric fraction were obtained.

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